Carbon Monoxide Detector

Related Applications

This application is a continuation of U.S. Patent Application Serial No. 10/208,601 filed 29 July 2002, which is a continuation under 35 U.S.C. 111(a) of International Application No.: PCT/GB01/00334 filed 29 January 2001 and published in English under Publication No. WO 01/55710 A1 on 2 August 2001, which claims priority from Great Britain Application No. 0002027.1 filed 28 January 2000 and Great Britain Application No. 0002808.4 filed 9 February 2000, which applications and publications are incorporated herein by reference.

The present invention relates to a method and an instrument for detecting carbon monoxide.

Carbon monoxide is an odourless, colourless, tasteless poisonous gas which can be produced by incomplete combustion of hydrocarbons. Gas fired domestic equipment such as water heaters, gas fires etc. can give off carbon monoxide when they are not functioning properly or when they are not properly maintained and checked. The emission of carbon monoxide can be fatal and there have been people killed by carbon monoxide poisoning in these circumstances, even levels of carbon monoxide below the lethal limit can cause headaches, nausea and illness due to carbon monoxide poisoning.

Apart from domestic situations, carbon monoxide can be emitted in industrial operations and is a component of the exhaust of internal combustion engines. The levels of carbon monoxide is a measure of air pollution and legal controls are imposed on carbon monoxide levels in air.

For these reasons accurate reliable carbon monoxide monitors are needed which can detect and monitor accurately low levels of carbon monoxide.

Existing types of carbon monoxide detectors can be broadly classified into one of

four types according to the gas sensitive element employed: chemical, electrochemical, semiconducting or spectroscopic (infra-red). The electrochemical and spectroscopic devices, whilst offering rapid response times, high resolution and high accuracy, are expensive and not suitable for domestic use. Chemical sensors are inexpensive devices that are usually based on palladium or iodine salts which exhibit a colour change upon exposure to CO. They are of two classes; tapes for continuous monitoring which can provide very fast and sensitive response (typically sub ppm concentrations are sensed) but these require very careful control over moisture content and tubes which are used for spot checks and are of generally lower sensitivity than tapes although they do not require such careful control of moisture. Both types rely on a colour change and could not be made "automatic" by the application of an electronic device the degree of colour change. These devices are not reusable. However, their response to low CO concentrations tends to be poor and therefore constant monitoring is required and can only be used once and fail to provide audible warning signals.

The most popular carbon monoxide detectors for domestic use utilise a gas sensitive semiconductor, the resistance of which changes upon exposure to a reducing gas. Of these the most popular material is SnO_2 and platinum doped SnO_2 other binary oxides include ZnO, TiO_2 and a combination of CuO and ZnO to form a heterocontact More recently the use of mixed metal oxide semiconductors for CO detection has been reported. These materials include the niobates $CrNbO_4$, $FeNbO_4$ and $Ba_6Fe_{1.5}Nb_{8.5}O_{30}$ and the perovskite $Lao_{0.5}Sr_{0.5}CO_3$.

However, three problems exist with the use of semiconducting metal oxides for CO detection these are:-

1. Low sensitivity to concentrations below approximately 100ppm, this being equally as applicable to high operating temperatures as it is to operation at room temperature.

2. Poor selectivity towards the gas desired for detection with respect to cross sensitivity with co-existing gases.

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3. Poor reproducibility of sensor characteristics, in particular due to the fabrication processes employed. The use of ESD, and related techniques, provides for greater control over fabrication and therefore sensor characteristics.

SnO_2 provides resistance changes upon exposure to a wide range of gases including, CO, CH_4 and H_2S. The problems of sensitivity and selectivity are commonly overcome by heating the semiconductor to approximately 200°C for response to CO. However, such heating is considered undesirable due to the power drain being too great for remote operation from batteries and a mains power supply is necessary and sensitivity can remain poor with respect to sub 100ppm levels even with heating to greater than 200°C.

We have now discovered a semiconducting oxide which exhibits appreciable resistance changes to CO concentrations below 100 ppm and is capable of operation at room temperature and which can be incorporated into CO detection units for domestic, industrial, medical and vehicular use.

According to the invention there is provided a method for the detection of carbon monoxide in air which comprises contacting the air with a sensor which incorporates an element formed from $Ni_xCo_{1-x}O_y$ (I) where x is from 0.1 to 0.9, and y is 4x, and measuring the change in the electrical properties of the element. Preferably, x is from 0.2 to 0.5 and y is from 0.8 to 2.0. When x is 0.33 and y is 4x a spinel structure is formed. When x is not 0.33 some spinel will be present which will be active but other oxides such as NiO and Co_3O_4 will also be present.

The invention also provides a device for detecting carbon monoxide levels in air, which device comprises a sensor element comprising a film or layer of (I) and a means able to measure a change in the electrical properties of the film or layer on exposure to carbon monoxide.

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Preferably (I) has a spinel structure and the stoichiometric formula of (I) is $NiCo_2O_4$, i.e., x is 0.33 and y is 4x, but in practice, (I) will have a formula which can be expressed as $Ni_xCo_{1-x}O_y$ with deviation from the exact formula giving a sensor which is less effective but which could be useful. This is indicated by the

5   change in resistance in air of the compound; the greater the resistance the greater the change in resistance being needed for a reliable detection signal and this is illustrated in fig. 1 in which it can be seen that at X = 0.33 there is the lowest resistance.

10 Depending on the method of formation, a film or layer of (I) will contain $NiCD_2O_4$ mixed with cobalt and nickel oxides to give a composition in which the ratio of the components deviate from the strict stoichiometric ratios.

    Any electrical property which changes on contact of the film with carbon monoxide
15 can be monitored e.g. the resistance, capacitance etc. A preferred property is the resistance and the resistance of (I) increases on exposure to carbon monoxide.

    A device according to the invention which utilises the change in resistance of (I) comprises a substrate on which there is an element which comprises a film or layer
20 of (I), attached to the element are electrodes and there is a means to measure the electrical resistance of the element.. The means to measure the resistance can be any conventional means, for example a small voltage is applied between the electrodes e.g. from a battery and the current flowing monitored.

25 The film or layer of (I) can optionally include graphite powder, preferably in an amount of 5 to 20% of the weight of the film or layer. The graphite powder should be uniformly dispersed in the film or layer and preferably has an average particle size below one micron.

30 When the element is exposed to carbon monoxide the resistance of the element increases and the current decreases, when the current decreases below a pre-set

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level, which indicates a level of carbon monoxide above a safe level, an alarm or warning can automatically be triggered. Alternatively the change in voltage at constant current can be used to evaluate the resistance change. In addition the device can be used to provide for the continuous detection of carbon monoxide. The device

5   can be adapted to provide for the continuous monitoring of carbon monoxide levels by means of circuitry which correlates the change in the resistance of the element with change in concentrations of carbon monoxide.

If the power supply should fail, a warning or alarm is automatically triggered as the

10   current drops and this a fail-safe feature against inoperation due to power failure.

In order to measure the resistance there are electrodes attached to the film or layer of (I) and it is important that there is a good electrical contact between the film and the electrodes so there is minimal resistance caused by the attachment of the

15   electrodes to the element.

Preferred electrodes can be formed of an inert metal such as gold, which has no electrical junction effects with the sensor element. The contact material itself should have no reaction with carbon monoxide.

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In order to compensate for the effect on resistance of temperature fluctuations a reference sensor can be used which is the same as the detecting sensor but which is hermetically sealed from the atmosphere and so sealed from the sensing environment. Both the sensors would be subject to the same temperature

25   fluctuations and so any difference in their resistances would be due solely to the presence of a reacting gas.

As changes in the electrical resistance of the element are measured, a low base resistance of the element is preferred so the change in resistance of the element

30   compared with the base resistance of the element is greater. This can be accomplished by having an element with a low specific resistivity and there being a

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short path length through the element between the electrodes. The resistance change required to give a reliable signal will depend on the particular circumstances and the electrical circuits used, but normally a resistance change of 25% is suitable although lower resistance changes can be used, particularly when a reference sensor is used to

5   compensate for temperature variation.

The film or layer of (I) can be prepared by known methods for example by thermal decomposition of solutions of the metal nitrates or hydroxides, spray pyrolysis, cryochemical deposition, co-precipitation of the metal oxides and electrostatic spray

10   deposition.

The preferred methods used are thermal decomposition and electrostatic spray deposition. However a printing technique, such as silk screen printing may also be applied using $NiCO_2O_4$ powder and a solution of metal salts followed by thermal

15   decomposition.

Electrostatic spray deposition is described in "A Review of Liquid Atomisation by Electrical Means" by J.M Grace and J.C.M. Marijinissen, ESF Workshop on Electrospraying. Sevilla 1997 and "Electrostatic Spray Deposition of Doped YSZ

20   Electrode Materials for a Monolithic Solid Oxide Fuel Cell Design" 10th IEA SOFC Workshop. Diablerets. Switzerland. 2 (1997) 236-247.

A preferred structure of the sensor of the present invention has a film of (I) deposited or formed on to a substrate such as foil or ceramic substrate. Preferably a

25   film of (I) is deposited on the substrate as it is formed e.g. by thermal decomposition of solutions of precursor metal salts such as metal nitrates or by electrostatic spray deposition e.g. of precursor metal salts such as metal nitrates.

The nature of the substrate is not critical and any suitable substrate can be used, for

30   example substrates which have physical properties similar to those of the deposited film.

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When thermal decomposition is used to form the film or layer, mixed cobalt and nickel nitrates are preferably thermally decomposed directly onto a substrate such as a nickel foil. Nickel has a coefficient of expansion similar to (I) so the risk of cracking etc. due to changes in temperature is reduced. The film or layer can be made by forming a gel of cobalt nitrate and nickel nitrate in stoichiometric ratio by evaporation of a solution of the mixed nitrates on the substrate and then drying and heating the gel at elevated temperature for example from 250°C to 650°C. e.g. 350°C to form the film or layer of compound (I) on the substrate.

The technique of Electrostatic Spray Deposition (ESD), developed at the University of Delft, provides an inexpensive and facile means of preparing thin films of inorganic substances. ESD has been successfully applied to production of a wide variety of thin films for solid oxide fuel cells, including those having a spinel structure.

ESD involves the production of an aerosol from a precursor solution through the application of a high positive potential to a metal capillary (nozzle), this being directed towards a heated, electrically grounded substrate. As the precursor solution is pumped through the capillary, droplets will grow at the tip of the nozzle.

The positive potential causes positive ions in the solution to migrate to the surface the droplet, resulting in a surface charge which causes an electrostatic pressure to oppose the surface tension of the liquid. Through the variation of electrode configuration, nozzle design and liquid properties (viscosity and conductivity) many spray modes, having widely different geometries, may be achieved.

A process of decomposition then occurs as charged droplets are subsequently attracted by coulombic forces to the grounded substrate. It is suggested that such decomposition occurs, together with solid state reaction of precursor cations, within the spray cone caused by the high potential being applied

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Conventional ESD can be used in the present invention.

Other techniques which can be used include flame assisted vapour deposition and electrostatically assisted vapour deposition.

Another method of preparing $NiCo_2O_4$ films onto metal substrates is by co-spraying $NiCo_2O_4$ films powder and solution together via electrostatic spraying or simply depositing the mixture and solution onto the substrate followed by thermal decomposition e.g. at 400°C or by use of printing techniques.

It is a feature of the sensors of the present invention that they are resistant to interference by other pollutant gases which are commonly present in the atmosphere such as oxides of nitrogen, referred to as NOx, and the sensors of the present invention work in the presence of such gases.

In general the sensors work better at higher temperatures, but unlike existing sensors the sensors of the present invention detect low levels of carbon monoxide at ambient temperatures. The sensors of the present invention are also relatively unaffected by changes in humidity.

The performance of the sensors of the present invention can be affected by the addition of other metals as surface and bulk additives to the compound (I). It was found that the addition platinum group metals e.g. palladium could improve the sensitivity, the levels of palladium used preferably range from 1 to 5% preferably 4 to 5%.

The invention is illustrated in the following Examples.

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Example 1

Nickel foil (99.9% Aldrich) had a film of (I) formed on it by a process in which the
foil substrate was coated three times with mixed cobalt and nickel nitrates from an
5   alcoholic solution, pressed under a 1 kg weight to equalise particle separation and
obtain uniformity of coverage and then fired at 400°C for 2 hours between each
successive coating. The loading thereby obtained was 3.2 g/cm^2. The resistance was
then measured along a linear profile on each surface via a two probe method using a
digital multimeter (Hewlett Packard 3478A) and the contact spacing measured to
10   two decimal places with a digital micrometer (Mitayoka). The relationship between
resistance and contact spacing was observed to be linear.

The sensors were evaluated for their response to carbon monoxide. Sensitivity is
defined as $(R_g-Ro)/Ro$ where R_g is the resistance in the contaminant gas and Ro is
15   the resistance in clean air.

A change in resistance of 25% was arbitrarily taken as a level which would be used
to trigger an alarm. The sensor was exposed to air containing various levels of
carbon monoxide and the time taken to register a 25% change in resistance
20   measured.

In exposure to air free of carbon monoxide the variation in resistance over a long
period of time (72 hours) was found to vary between 0.25 and 0.6% of the initial
value and in exposure to air with background levels of carbon monoxide (1 ppm) the
25   resistance was found to vary by -1.4 to +3.5 % of the initial value thus indicating
that there was little risk of false positives being found.

The sensor was exposed to a carbon monoxide concentration of 10 ppm and the
resistance measured against time, a change in sensitivity of 3 indicates a 25%
30   change in resistance. The results and the result for exposure to background level of
1ppm carbon monoxide is shown in fig. 2, as can be seen the warning level was

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attained after 75 mins. Existing semiconductor sensors cannot detect carbon monoxide levels of this order at ambient temperatures.

This was repeated for carbon monoxide concentrations of 35ppm to 400ppm, 500 to 1000ppm and for 5000ppm to 2% and the results shown in figs 3, 4 and 5.

The recovery of the sensor when the levels of carbon monoxide were reduced to background levels was also measured and the results shown in figs 6, 7 and 8. As can be seen the resistance was quickly reduced to its base level.

The sensors were evaluated for sensitivity to NOx as a pollutant gas which is found some exhaust gases which contain carbon monoxide and it was found that there was no decrease to the selectivity to carbon monoxide on exposure to NOx in the concentrations likely to be found.

Example 2 Electrostatic spray deposition.

A ceramic substrate of 96% alumina having screen printed gold electrodes (Du Pont plc) was cut to the dimensions shown in Fig. 9 which illustrates an example of a sensor substrate coated with $NiCo_2O_4$ using electrostatic spray deposition under a range conditions to prepare a number of samples and the conditions used are shown in Table 1.

Table 1

Sample	Precursor flow rate ml/hr.	Precursor Molarity M	Substrate Temperature °C	Deposition Time hours	Applied Potential kV	Loading mg/cm²
1	0.55	0.05	375	4	17.77	0.5
2	0.57	0.05	493	2	10.47	0.27
5	0.55	0.05	445	2	15.75	0.29
6	0.57	0.05	402	2	12.20	0.3
7	0.55	0.05	445	1	15.57	0.11
8	0.57	0.05	448	4	11.87	0.54
9	0.55	0.05	303	4	17.31	0.48
10	0.57	0.025	400	2	10.39	0.13
14	0.55	0.025	349	2	17.6	0.17
15	0.57	0.025	373	2	9.82	0.14
16	0.55	0.05	393	2	17.19	0.29
17	0.57	0.025	372	2	10.23	0.14

The Solvent was 20vol% absolute alcohol and 80vol% butyl carbinol (Di(ethylene glycol)butyl ether, (99% Aldrich).

The resistance of the samples and the sensitivity to carbon monoxide levels of 100ppm for 1 hour as shown by the response time to achieve a 25% increase in resistance were measured as described in Example 1 and the results shown in Table 2

Table 2

Sample	Response Time Mins.	Base Resistance k ohms
1	60	1.52
2	45	4.24
5	20	4.20
6	50	2.88
7	20	4.36
8	30	2.22
9	20	1.40
10	40	2.52
14	30	4.60
15	30	2.44
16	30	1.12
17	20	0.28

As can be seen the sensors of the present invention can detect carbon monoxide from low levels at ambient temperatures.

Example 3

Sensor samples prepared using spray pyrolysis with and without the addition of 5% palladium and the percentage increase in resistance after 30 mins exposure time to 100ppm of carbon monoxide was measured at temperatures from 50°C to 200°C and the results shown in Table 3 which show sensitivity values.

Table 3

Sensor	50°C	100°C	150°C	200°C
$NiCo_2O_4$	9	7	10	13
$NiCo_2O_4$ + Pd	8	18	26	36

As can be seen the addition of the palladium increases the sensitivity.